

POLYETHYLENE DEGRADATION IN A COAL LIQUEFACTION ENVIRONMENT

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INTRODUCTION

The coprocessing of coal with waste materials such as plastic has shown promise as an economical means to recover the inherent value of the wastes while producing useful products. Polyethylene (PE) is one of the dominant plastic materials; recent statistics indicate that low- and high-density PE together make up about half of all municipal plastic waste.¹ The degradation of PE in a pyrolysis environment has been well studied,² and pyrolysis-based methods for the conversion of PE to fuels have been published.³ However, recent studies have shown that PE is among the most difficult plastics to convert in the traditional liquefaction environment, particularly in the presence of coal and/or donor solvents.⁴ The coal liquefaction environment is quite different than that encountered during thermal or catalytic pyrolysis. Understanding the degradation behavior of PE in the liquefaction environment is important to development of a successful scheme for coprocessing coal with plastics.

In this paper, a novel analytical method has been developed to recover incompletely reacted PE from coprocessing product streams. Once separated from the coal-derived material, gel permeation chromatography, a conventional polymer characterization technique, was applied to the recovered material to ascertain the nature of the changes that occurred to the PE upon processing in a bench-scale continuous liquefaction unit. In a separate phase of the project, 1-L semi-batch reactions were performed to investigate the reactivity of PE and coal-PE mixtures as a function of temperature.

EXPERIMENTAL SECTION

Materials. Liquefaction experiments were conducted using -200 mesh Black Thunder mine coal (Wyodak-Anderson seam, Campbell County, WY). High-density polyethylene (PE; $T_m = 135^\circ\text{C}$, $d = 0.96\text{ g/mL}$) was supplied by Solvay Polymers. Polystyrene (PS; $T_m = 95^\circ\text{C}$, $d = 1.0\text{ g/mL}$) was supplied by BASF. Polypropylene (PP; $T_m = 176^\circ\text{C}$, $d = 0.94\text{ g/mL}$) was supplied by Amco Plastics. The same plastics were used in both the semi-batch experiments and the bench-scale continuous run. All plastics were supplied as 3.2 mm (0.125 in) extruded pellets. A mildly hydrogenated petroleum-derived oil, containing small amounts of coal derived liquid, was used as a solvent in the semi-batch coprocessing tests. The bench scale continuous unit run was started up on a similar solvent but then operated in a recycle mode. An aged Ni-Mo catalyst supported on alumina in the form of 1/16" extrudates (AO-60) was supplied by Akzo and used in the semi-batch tests. Both molybdenum and iron based catalysts were used in the bench-scale continuous run. Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) solvents used in work up and/or extraction procedures were obtained in bulk grade and used without further purification. Decane fraction (bp $171\text{--}177^\circ\text{C}$), used in the PE recovery procedure, was obtained from Fluka Chemie AG and used without further purification.

Reactions. Semi-batch tests were performed in a 1-L stirred-tank reactor system.⁵ Sample work-up and feed conversions were calculated by a procedure described previously.⁶ Samples were obtained from a bench scale continuous mode run performed on a close-coupled, two-stage, catalytic reactor system, and operating as part of the U.S. Department of Energy's coal liquefaction program. A simplified schematic diagram of the continuous unit configuration is shown in Figure 1. Samples were obtained from the following points, identified in Figure 1: (1) feed slurry, (2) first reactor, (3) second reactor, (4) atmospheric still bottoms, (5a) vacuum still overhead, and (6a) vacuum still bottoms, or (5b) pressure filter liquid, and (6b) pressure filter solids. Samples were taken during three different coprocessing run conditions, identified by the feed type: (1) coal mixed plastics in a 2:1 ratio (67% coal, 13% PE, 11% PP, 9% PS), (2) coal:PE in a 2:1 ratio, and (3) coal:plastics in a 1:1 ratio (50% coal, 20% PE, 16.5% PP, 13.5% PS).

Extraction of Incompletely Reacted PE from Bench Scale Continuous Unit Process Streams. In order to more thoroughly investigate the behavior of PE in a coal liquefaction system, a general method was devised to recover incompletely reacted PE

from coal liquefaction process streams. The method is diagrammed in Figure 2. The first step involved a cold THF wash to remove as much soluble coal-derived material as possible without affecting the incompletely reacted PE. In fact, this step alone was sufficient to isolate PE from a tarry stream that contained no insoluble coal matter (e.g., a non-ashy recycle stream).⁷ The THF insolubles were then subjected to a hot decane extraction; the decane fraction dissolved the incompletely reacted PE, but left the coal derived solids behind. After the hot decane was filtered and concentrated, a dichloromethane wash was used to remove any remaining coal derived materials and aid in formation of an beige, powdery solid. The method also removes other polyolefins, such as PP. The method was applicable to a wide range of process streams including tars, solids, and multi-phase mixtures.

The process samples containing unreacted PE existed either as solids or as viscous tars. If solid, the sample was crushed in a mortar and pestle prior to the extraction procedure. If tar, the sample was heated in an oven at low temperature (<100°C) and poured into a reaction flask. The procedure began by digesting the solid co-processing residue in THF. The sample (5-25 g) was placed into a Whatman cellulose Soxhlet thimble (25 mm od x 100 mm), submerged in THF (ca. 250 mL) within a beaker and sonicated for about 1 hr at ambient temperature. At this point the THF solution had turned dark brown with soluble coal-derived material. After the THF was removed, the thimble was placed in a Soxhlet extraction apparatus and exhaustively extracted with another 500 mL of fresh THF. This extraction typically required 24 hr before the washings become colorless.

The THF insoluble material (at this point typically 1-10 g) were vacuum dried inside the extraction thimble in an oven at 50°C to evaporate any residual THF, then transferred to a 500 mL flask along with ca. 300 mL decane fraction (bp 171-177°C), used as received from Fluka Chemie AG. The mixture was refluxed under flowing nitrogen (preventing atmospheric oxygen from coming into contact with the hot decane solution) for 1 to 2 days to digest the PE. The *boiling hot* decane solution was then filtered through a fresh cellulose Soxhlet thimble (43 mm od x 125 mm) to give a black solid and a viscous yellow filtrate containing the incompletely reacted PE. The decane was evaporated under reduced pressure on a rotary evaporator at 70°C to yield a yellow to yellow-brown filmy residue which adhered to the walls of the flask.

After addition of ca. 300 mL CH_2Cl_2 , the residue was then scraped from the walls of the flask and sonicated at ambient temperature for 1 hr. After sonication the CH_2Cl_2 had become yellow and the residue had formed flocculent particles and flakes. The mixture was filtered through a medium-porosity glass frit to give a light beige to tan solid and yellow CH_2Cl_2 filtrate. The beige incompletely reacted PE product was vacuum dried in an oven at 50°C until constant weight.

Gel Permeation Chromatography (GPC). GPC of the recovered PE samples was performed by Jordi Associates, Inc., of Bellingham, MA. Samples were dissolved in trichlorobenzene at 145°C, and analyzed on a Waters 150C high pressure liquid chromatograph, equipped with a mixed bed linear column (prepared at Jordi) and refractive index detector. Calibration was done with polystyrene standards. Molecular weight distribution parameters M_n , the number average molecular weight, and M_w , the weight average molecular weight, were provided by the data acquisition and handling software at Jordi. For convenience in interpreting samples with bimodal molecular weight distributions, the maximum points in the distribution curves (i.e., the most frequently occurring molecular weight values) were calculated at PETC.

RESULTS AND DISCUSSION

The efficacy of a coal liquefaction procedure is generally measured in terms of conversion, usually defined in terms of solubility in a given solvent or distillation at or below a given endpoint. Although this is a functional way of evaluating a set of processing parameters, it reveals little about the chemical nature of the species involved in the reactions. The ability to isolate and recover unconverted PE from a coal-plastics coprocessing stream affords the ability to characterize it without the complexity of the coal and coal derived products. This yields a significant opportunity to understand the degradation of PE in the coal liquefaction environment.

The PE recovery method was developed at PETC according to the procedure diagrammed in Figure 2 and described in the Experimental Section. The method was

tested on a sample of virgin PE ($M_n = 15,000$; $M_w = 100,000$) of the same source as was used as feed in the semi-batch and bench-scale continuous runs. The percentage of original PE recovered, and the GPC data for the virgin PE before and after the extraction procedure is shown in the first two lines of Table I. None of the initial PE was left behind; the recovery of 86% represents losses that occurred upon the filtration step due to rapid cooling of the decane solution. A better hot filtration method is currently being implemented to improve quantitation of the technique. The slightly higher molecular weight values of the PE obtained after extraction may indicate the occurrence of condensation reactions during extraction; this observation is currently being investigated.

The PE extraction technique was also tested by examining a coprocessing sample (containing both coal and PE) before and after PE extraction, using solid state nuclear magnetic resonance (NMR) spectroscopy done by Ronald Pugmire and Mark Solum at the University of Utah.⁹ Before extraction, the aliphatic portion of the spectrum consisted of a single sharp peak in the CH_2 region superimposed on a broader signal due to coal-derived material. After extraction, the recovered PE yielded only the sharp CH_2 signal; the coal-derived residue materials showed only the broader signal.⁹ Thus it is reasonable to assume that, except for filtration losses, the method removes essentially all of the incompletely reacted PE and no coal derived material.

The extraction technique was used to recover PE from a series of sampling streams during three different feed conditions of a coprocessing operation on a bench scale continuous unit. The percentage of each sample stream recovered, as well as the molecular weight distribution parameters obtained from GPC of the recovered material, are listed in Table I. Molecular weight distribution curves, obtained from GPC data for the 2:1 coal:PE feed condition, are shown in Figure 3a-e. For comparison, a GPC trace of the unreacted PE after extraction is shown in Figure 3f.

The most dramatic observation from Figure 3 is the presence of two peaks in the samples taken from the feed slurry (Figure 3a) and first reactor (Figure 3b). The two peak maxima occur at molecular weight values of approximately 2,000 and 50,000 amu. The larger maximum in Figure 3a (and 3b) strongly resembles the unreacted, extracted PE in Figure 3f. Therefore, the larger, or higher molecular weight peak in Figure 3a (and 3b) can be assigned to fresh PE feed. The smaller, or lower molecular weight peak in Figure 3a (and 3b) resembles the PE recovered from the sampling points downstream in the process (Figure 3d,e). In particular, the PE-containing pressure filter liquid stream (Figure 3e) constituted the recycle vehicle during the 2:1 coal:PE operating condition of the continuous unit. Therefore the peak at about 2,000 amu in Figure 3a (and 3b) can be attributed to PE that had been recycled back to the feed slurry after having been through the process. In the other two feed conditions listed in Table I, the sample from the feed slurry (and first reactor) also exhibits bimodal distributions. The feed slurry and first reactor samples also contain unreacted PP, but the same conclusions are valid. This is the first time that a method exists to unambiguously distinguish PE that has been recycled through the process to that has been freshly added to the feed.

Downstream of the feed slurry, the distribution of recovered PE remains bimodal into the first reactor (Figure 3b, Table I). However, by the sampling point for the second reactor (Figure 3c), the bimodal distribution is gone. The GPC molecular weight distribution shows only a single peak, with a maximum and an M_n value approaching that found in the downstream samples (Figure 3d, Table I). This observation confirms that most of the PE breakdown occurs in the reactor zones, i.e., between the sampling points for the first and second reactors. A gradual narrowing of the lineshape from the second reactor (Figure 3c) to the atmospheric still bottoms sample (Figure 3d) and pressure filter liquid (Figure 3e) with accompanying reduction in molecular weight seen in Table I is indicative that some PE breakdown continues past the reactor section of the unit. The same argument can be made for the 2:1 coal:plastics and 1:1 coal:plastics feed conditions (Table I). Thus, it appears that most, but not all, of the PE degradation takes place in the reactor zone.

An important point that should not be overlooked in this finding is that virtually all of the PE feed material *has* undergone some degree of reaction. Because conventional solubility tests or distillation procedures in coprocessing experiments have indicated that PE is difficult to convert, it is easy to make the erroneous assumption that the unconverted PE is also unreacted. These experiments show conclusively that such is not the case. The molecular weight of the PE feed has been reduced by a factor of 10 to 30, depending on what parameter is used to characterize the molecular weight

distribution. The recovered PE has simply not reacted sufficiently to be considered to be converted by traditional coal liquefaction measures.

Two different methods of solids separation were used on the atmospheric still bottoms stream during the continuous run. During the 2:1 coal:plastics feed condition, vacuum distillation was employed. In this configuration no PE was found in the vacuum still overhead material; it all went with the solids. Therefore, a recycle stream produced from only vacuum distilled material would be free of incompletely reacted PE. (In actuality, the recycle stream during the 2:1 coal:plastics condition was a combination of vacuum still overhead and atmospheric still bottoms; hence the PE in the recycle stream.) During the 2:1 coal:PE and 1:1 coal:plastics feed conditions, pressure filtration was employed on the atmospheric still bottoms. In this configuration, most of the unconverted PE went with the filtrate; only a small, approximately constant amount was recovered with the solids. The pressure filtration was done at a temperature above the melting point of PE so most of the PE passed through the filter as liquid or in solution; a small amount became entrained and trapped in the filter cake. Therefore, a recycle stream produced from pressure filtered material would be high in incompletely reacted PE. In this way, the method of solids separation could be tailored to retain or exclude incompletely reacted PE from the recycle stream.

In a separate aspect of the project, 1-L semi-batch reactions were performed to investigate methods for optimizing PE conversion and overall feed conversion in coal-plastics coprocessing. The effect of temperature on the conversion three different feed mixtures to <850°C distillable products is illustrated in Figure 4. The results from a 1:1 ratio of coal:mixed plastics, a 1:1 ratio of coal:PE, and PE feed alone are compared at 430°C, 445°C, and 460°C. The conversion of 1:1 coal:mixed plastics increases from 430°C to 445°C, then levels out from 445°C to 460°C. The conversion of 1:1 coal:PE increases fairly steadily across the entire temperature range. The conversion of the PE only feed shows the most significant increase between 445°C and 460°C. Although the conversion of all three feed mixtures increase with temperature, the PE, at least when used without coal or other plastics, seems to be influenced most by increasing the temperature from 430°C to 460°C. The results suggest that temperature is an important parameter in processing of PE under coal liquefaction conditions. This study will be continued by applying the PE extraction method discussed earlier to the incompletely reacted PE from these semi-batch runs, in order to determine how the temperature or feed composition influences the nature of the PE left unconverted.

Summary. A novel method has been developed to isolate and recover incompletely reacted PE from coal-plastics coprocessing product streams. The method has been applied to samples obtained from a bench scale continuous unit and the recovered material has been characterized by gel permeation chromatography. The method has conclusively established that virtually all PE undergoes some reaction in the coal liquefaction environment, with an average reduction in molecular weight distribution for the "unconverted" material of 10 to 30. The method can definitively distinguish between fresh (feed) and recycled PE in the process stream, and has established that most of the PE degradation occurs in the reactor zone. Vacuum distillation and pressure filtration have dissimilar effects on the incompletely reacted PE present in the atmospheric still bottoms process stream. Finally, semi-batch studies demonstrate the influence of temperature on the distillate conversion of various coal and plastics feed combinations.

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DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

REFERENCES

1. Smith, R.A. "Overview of Feedstock Recycling of Commingled Waste Materials," Ninth Annual Technical Meeting, Consortium for Fossil Fuel Liquefaction Science, Pipestem, WV, August 15-18, 1995.
2. Madorsky, S.L. "Thermal Degradation of Organic Polymers," Polymer Reviews Volume 7, Mark, H.F., Immergut, E.H., Eds.; Wiley-Interscience: New York, 1964; pp 93-129.
3. Ng, S.H. *Fuel*, **1995**, 9, 735-742.
4. (a) Palmer, S.R.; Hippo, E.J.; Tandon, D.; Blankenship, M. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.*, **1995**, 40(1), 29-33. (b) Huffman, G.P.; Feng, Z.; Mahajan, V.; Sivakumar, P.; Jung, H.; Tierney, J.W.; Wender, I. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.*, **1995**, 40(1), 34-37.
5. Cugini, A.V.; Krastman, D.; Lett R.G.; Balsone, V.D. *Catal. Today*, **1994**, 19(3), 395-408.
6. Cugini, A.V.; Rothenberger, K.S.; Ciocco, M.V.; McCreary, C. In *Coal Science, Proceedings of the Eighth International Conference on Coal Science, Volume II*, Pajares, J.A.; Tascon, J.M.D., Eds.; Coal Science and Technology Series, Volume 24; Elsevier: Amsterdam; 1995; pp 1299-1302.
7. Robbins, G.; Pradhan, V., personal communication
8. Pugmire, R.; Solum, M., personal communication

Figure 1: Simplified diagram of continuous unit configuration.

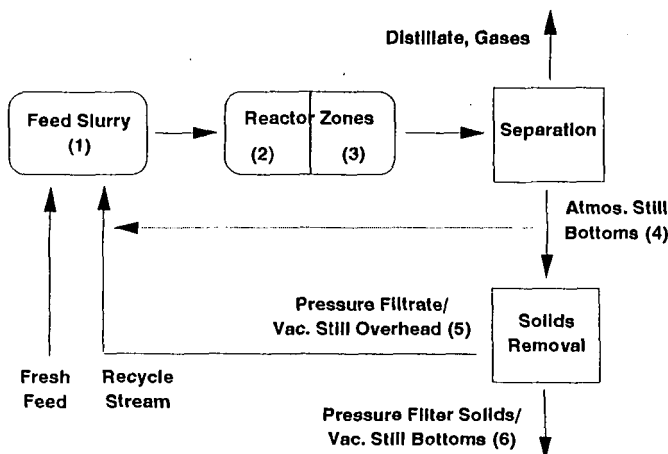
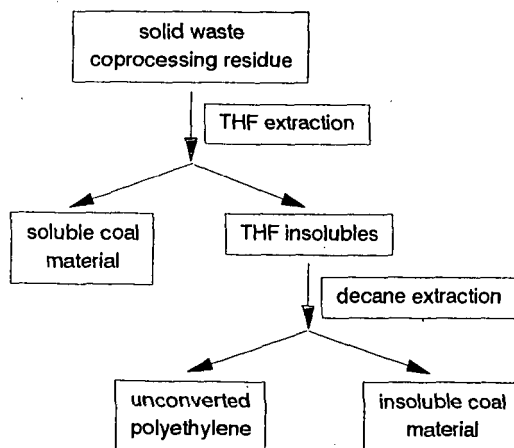


Figure 2: Scheme for recovery of incompletely reacted PE.



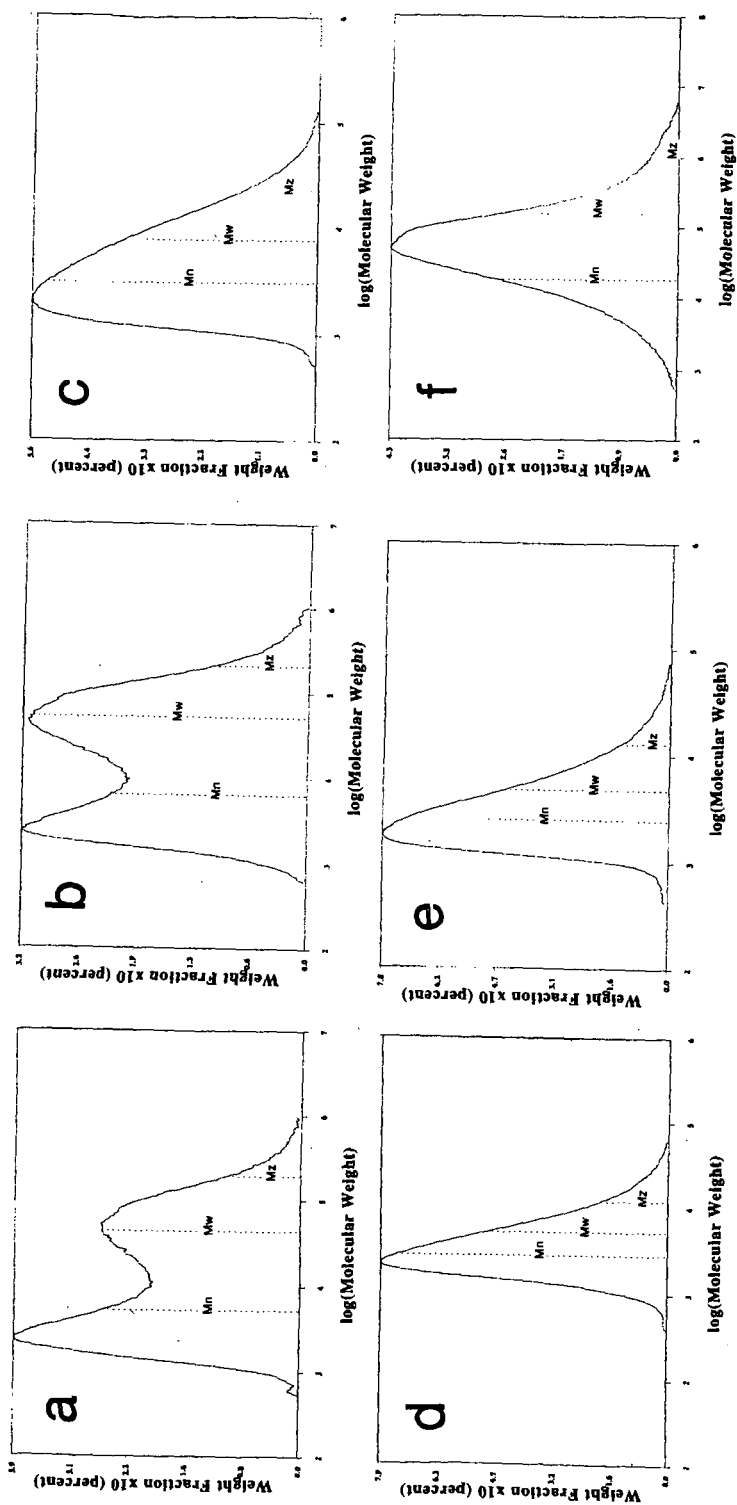


Figure 3: GPC data for 2:1 coal:PE feed condition. (a) feed slurry [sample stream 1], (b) first reactor [2], (c) second reactor [3], (d) atmospheric still bottoms [4], (e) unreacted, pressure filter liquid [5b], (f) extracted PE.

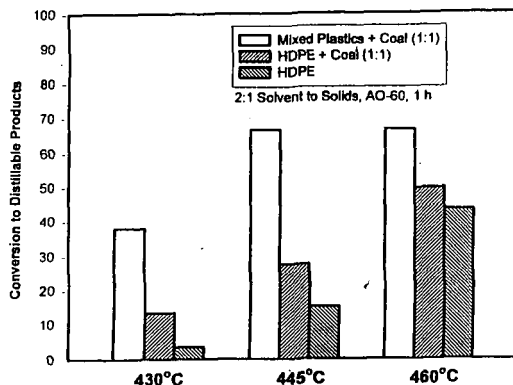


Figure 4: Effect of Temperature on Conversion to Distillable Products (Semi-Batch Studies)

Table I. GPC Results for PE Recovered from Continuous Bench Scale Unit.

Sample Description	PE yield ^a	Max ^b	M _n ^b	M _w ^b
Unreacted Polyethylene (PE)				
PE before extraction	----	46,000	15,000	100,000
PE after extraction	86 %	54,000	19,000	150,000
2:1 coal:plastics condition				
(1) feed slurry	8 %	2,500; 85,000	9,700 ^c	230,000 ^c
(2) reactor #1	8 %	1,900; 96,000	8,000 ^c	200,000 ^c
(3) reactor #2	3 %	2,400	3,400	8,000
(4) atmospheric still bottoms	3 %	2,000	2,500	4,100
(5a) vacuum still overhead	0 %	----	----	----
(6a) vacuum still bottoms	12 %	1,500	1,900	3,100
2:1 coal:PE condition				
(1) feed slurry	11 %	2,500; 47,000	5,000 ^c	42,000 ^c
(2) reactor #1	14 %	2,500; 50,000	6,200 ^c	51,000 ^c
(3) reactor #2	12 %	2,200	3,000	7,500
(4) atmospheric still bottoms	12 %	2,500	2,800	5,100
(5b) pressure filter liquid	18 %	1,800	2,400	4,800
(6b) pressure filter solids	2 %	1,400	1,900	3,500
1:1 coal:plastics condition				
(1) feed slurry	16 %	2,600; 76,000	3,000 ^c	160,000 ^c
(2) reactor #1	17 %	2,200; 80,000	2,700 ^c	120,000 ^c
(3) reactor #2	NA	NA	NA	NA
(4) atmospheric still bottoms	9 %	2,000	2,300	4,100
(5b) pressure filter liquid	10 %	1,300	1,300	1,500
(6b) pressure filter solids	2 %	1,300	1,700	2,900

a. This value represents the amount of PE reclaimed based on the total mass of the sample, not on the amount of PE originally located in the sample.

b. All data points except unreacted PE represent an average of two determinations. Unreacted PE value is based on a single determination.

c. Single M_n and M_w values were calculated by the GPC software based on the composite bimodal lineshape. Maxima were determined for each individual peak when more than one peak was present.